Phase Transformation of 10Li$_2$O-9MnO$_2$-16Fe$_2$O$_3$-15CaO-5P$_2$O$_5$-5Al$_2$O$_3$-40SiO$_2$ Glass

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Abstract

The phase transformation and magnetic properties of 10Li$_2$O-9MnO$_2$-16Fe$_2$O$_3$-15CaO-5P$_2$O$_5$-5Al$_2$O$_3$-40SiO$_2$ (LMFCPAS) glass have been observed and investigated using x-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive x-ray spectrometry (EDS), and transmission electron microscopy (TEM) with selected area electron diffraction (SAED). After crystallization of the LMFCPAS glass at 800 °C for 2 h, the crystalline phases of Li$_2$Al$_2$Si$_3$O$_{10}$, Li$_2$SiO$_3$, β-wollastonite (β-CaSiO$_3$), lithium orthophosphate (Li$_3$PO$_4$), magnetite (Fe$_3$O$_4$), and triphyllite (Li(Mn$_{0.5}$Fe$_{0.5}$)PO$_4$) were obtained. When the LMFCPAS glass crystallized at 850 °C, the β-wollastonite exhibited lath form morphology. As the LMFCPAS glass crystallized at 850 °C for 16 h and under an applied magnetic field of 1000 Oe, very small remnant magnetic induction and coercive force of 0.01 emu/g and 50 Oe were obtained, respectively.

Keywords: LMFCPAS glass, crystallization behavior, lath form

I. Introduction

The developments of ferromagnetic glass-ceramics such as CaO-SiO$_2$-P$_2$O$_5$-Fe$_2$O$_3$$^1$, CaO-SiO$_2$-P$_2$O$_5$-Na$_2$O-Fe$_2$O$_3$$^{2,3}$, Li$_2$O-Al$_2$O$_3$-SiO$_2$-Fe$_2$O$_3$-P$_2$O$_5$$^4$, and CaO-SiO$_2$-(Fe, Fe$_2$O$_3$)$$^5$ glasses by means of well-controlled crystallization processing have been reported previously. Some other studies attempted to change the matrix glass compositions by partially replacing oxides with MgO and ZnO$$^9,10$, or BaO and B$_2$O$_3$$^{11,12}$. In 2011, Ferreira da Silva and Costa$$^9$ demonstrated that the amount and type of preferential nanocrystalline zinc ferrite in Fe$_2$O$_3$-ZnO-MgO-SiO$_2$ crystallized glasses were affected by the glass compositions and heat treatment temperature. Mirkazemi et al.$$^{11}$ also reported that the crystallization phases of BaB$_2$O$_4$ and BaFe$_{12}$O$_{19}$ appeared when 45BaO-25Fe$_2$O$_3$-30B$_2$O$_3$ glasses powders were crystallized at 702 °C for 1 h. Their report also pointed out that BaB$_2$O$_4$ appeared first and subsequently the BaFe$_{12}$O$_{19}$ particles formed within the Ba$_2$B$_2$O$_4$-rich regions, which serve as suitably heterogeneous nucleation sites for their formation.

The crystallization kinetics of the Li$_2$O-MnO$_2$-Fe$_2$O$_3$-CaO-P$_2$O$_5$-SiO$_2$ glass systems using a non-isothermal method have been studied by Hsi et al.$$^6,7$. In addition, the crystallization kinetics and magnetic properties of iron oxide addition to 25Li$_2$O-8MnO$_2$-20CaO-2P$_2$O$_5$-45SiO$_2$ glasses have also reported by Hsi et al.$$^8$. The phase of (Li, Mn) ferrite was also reported to appear in this glass system after crystallization treatment. To avoid the appearance of (Li, Mn) ferrite in the Li$_2$O-MnO$_2$-Fe$_2$O$_3$-CaO-P$_2$O$_5$-SiO$_2$ glass systems, the Li$_2$O content in the glass composition needs to be reduced, but the Fe$_2$O$_3$ content and the addition of Al$_2$O$_3$ need to be increased in the glass composition, which eventually formed the 10Li$_2$O-9MnO$_2$-16Fe$_2$O$_3$-15CaO-5P$_2$O$_5$-5Al$_2$O$_3$-40SiO$_2$ glass (hereafter abbreviated to LMFCPAS glass).

This paper intends to report on the phase transformation and magnetic properties of the LMFCPAS glass, which has been studied in detail. X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive x-ray...
spectrometry (EDS), transmission electron microscopy (TEM), selected area electron diffraction (SAED) were applied to investigate the phase transformation of LMFCPAS glass. In addition, a superconducting quantum interference device (SQUID) was used for measuring the magnetic properties of crystallized LMFCPAS glass. The purpose of this investigation was first to study the phase transformation of LMFCPAS glass, second to examine the microstructure of crystallized LMFCPAS glass and finally to evaluate the magnetic properties of crystallized LMFCPAS glass.

II. Experimental Procedure

(1) Sample preparation

The reagent grade powders of Li2CO3, MnO2, CaHPO42H2O, CaCO3, Al2O3, and SiO2 with purity higher than 98% supplied by Nihon Shiyak Industries, LTD., Osaka, Japan, and Fe2O3 supplied by Kanto Chemical Co., Inc., Tokyo, Japan were used for preparing LMFCPAS glass. The weight percentage of Li2O, MnO2, Fe2O3, CaO, P2O5, Al2O3, and SiO2 in the glass was 10.0%, 9.0% 16.0%, 15.0%, 5.0% and 40.0%, respectively. All samples obtained in 50 to 100 g batches with specified composition were accurately weighed and respectively. All samples prepared for SEM observation were polished, etched with diluted acid solution (5 parts HF, 2 parts HCl and 93 parts distilled water) and coated with a thin layer of a conductive film. Thin foils for a transmission electron microscope (TEM, Hitachi HF-2000, Tokyo, Japan) were prepared with the conventional technique: the sample was sliced to a thickness of about 200 μm with a diamond-embedded saw, and then lapped mechanically to a thickness of about 30 μm and ion-beam thinned to electron transparent.

After it had been annealed, the LMFCPAS glass was cut into the lath shape with the length and width of 5 cm and 1.5 cm, respectively. The lath samples were crystallized at various temperatures for different durations, and then the LMFCPAS glass ceramics were obtained.

(2) Sample characterization

The crystalline phases of LMFCPAS glass-ceramics were identified with an x-ray diffractometer (XRD, D-MAX III B, Rigaku, Japan) with Cu Kα radiation and a Ni filter. The operating voltage and current were 30 kV and 20 mA, respectively, at a scanning rate (2θ) of 0.25°/min from 10° to 60°. A scanning electron microscope (SEM, Hitachi S-2700, Japan) was used to observe the crystallized samples. Chemical microanalysis was conducted with an energy-dispersive x-ray spectrometer (EDS, Noran 432 C, USA). All samples prepared for SEM observation were polished, etched with diluted acid solution (5 parts HF, 2 parts HCl and 93 parts distilled water) and coated with a thin layer of a conductive film. Thin foils for a transmission electron microscope (TEM, Hitachi HF-2000, Tokyo, Japan) were prepared with the conventional technique: the sample was sliced to a thickness of about 200 μm with a diamond-embedded saw, and then lapped mechanically to a thickness of about 30 μm and ion-beam thinned to electron transparent.

The TEM accelerating voltage was 200 kV. Selected area electron diffraction (SAED) examinations were performed on carefully thinned foils of the crystallized samples. Magnetic measurements were conducted using a superconducting quantum interference device (SQUID) magnetometer with the applied field up to 6 T.

III. Results and Discussion

(1) Crystallization behavior of the LMFCPAS glass

The effect of the crystallization temperature on the progressive development of phase transformation was studied based on the XRD patterns of the LMFCPAS glass crystallized at various temperatures for 2 h as shown in Fig. 1. It is found that (a) the glassy state was still maintained up to 700 °C as shown in Fig. 1(a). In comparison with the JCPDS database, the lithium aluminosilicate (Li2Al2Si3O10) (JCPDS Card No.25–1180), β-wollastonite (β-CaSiO3) (JCPDS Card No.42–547) and lithium orthophosphate (Li3PO4) (JCPDS Card No.84–0046) phases appeared in the LMFCPAS glass specimen crystallized at 750 °C as shown in Fig. 1(b). It is worth noting that diffraction peaks of the magnetite (FeFe2O4) (JCPDS Card No.19–627) also appear in this XRD pattern but the intensity is still weak. The XRD pattern of LMFCPAS glass crystallized at 800 °C as shown in Fig. 1(c) reveals the appearance of lithium silicate phase (Li2SiO3) (JCPDS Card No.29–829). The notably sharp diffraction peaks shown in Fig. 1(c) indicate that there are Li2Al2Si3O10, β-wollastonite, Li3PO4 and FeFe2O4 phases. In addition, a minor crystalline phase of triphylite [Li(Mn0.5Fe0.5)PO4] (JCPDS Card No.11–456) also shows up. Fig. 1(d) shows that the phases obtained in the specimen crystallized at 850 °C are similar to those crystallized at 800 °C.

![Fig. 1: XRD patterns of the LMFCPAS glass crystallized at various temperatures for 2 h.](image)
ceramics by Hsi et al. 8. They pointed out that when the LMCPS glass without the addition of Fe2O3 was heat-treated at 720 °C, the glass-ceramic contained LiMn2O4, β-CaSiO3, Li2Ca3Si4O12, and Ca(Ca, Mn)2Si2O5 phases. However, the (Li, Mn) ferrite gradually formed and became the minor phase for the LMCPS glass crystallized at 720 °C with extra addition of 4 at% and 8 at% Fe2O3. With the addition of extra Fe2O3, it was also shown that the LiMn2O4 became the minor phase for crystallization at 850 °C but the rest of crystalline phases shown in this LMCPS glass sample were the same as those crystallized at 720 °C without the addition of Fe2O3. It was clear that as the amount of Fe2O3 addition increased, the (Li, Mn) ferrite became more evident but the LiMn2O4 phase gradually decreased and finally started to form the Li2FeMn3O8 phase as the amount of Fe2O3 added reached 8 at% 8.

In a comparison of the phase transformation behavior of the present results with the previous study 8, it was found that crystalline phases observed in two studies are quite different except the β-wollastonite. The main reason for such discrepancy is that compositions for these two glass systems are quite different. The glass composition of previous study 8 contained 25 at% Li2O; the high content of Li2O might benefit the decrease in viscosity of the glass and the formation of Li2MnO4 at 600 °C. However, there was only 10 wt% Li2O in the glass system of this study; the sample could still maintain the amorphous state for LMFCPAS glass crystallized at 700 °C for 2 h. Furthermore, the magnetite, triphylite and lithium aluminosilicate phases were shown in the present study, but not the (Li, Mn) ferrite.

In addition, the 4.5MgO-(45-x)CaO-34SiO2-16P2O5-0.5CaF-xFe2O3 (5 wt% ≤ x ≤ 20 wt%) glass crystallized at 1050 °C for 3 h have been closely studied by Singh and Srinivasan 13. They pointed out that the crystalline phases of hydroxyapatite, wollastonite and magnetic appeared in all glass-ceramic samples. The additional phase of akermanite (Ca3MgSi2O7) was developed in the glass-ceramic samples when the glass composition of Fe2O3 was greater than 10 wt%. Singh et al. 3 also pointed out that the hydroxyapatite (Ca10(PO4)6(OH)2), magnetite and wollastonite were the major phases in 41CaO-(52-x)SiO2-4P2O5-xFe2O3-3Na2O (2 ≤ x ≤ 10 mol%) glasses heat-treated at 1050 °C for 3 h. In a comparison with the results from present work and that of the Singh et al. 3, it is found that most of the crystalline phases that appeared in these two recrystallized glass systems are different except the magnetic and wollastonite phases 3,13. The different crystalline phases in two glass systems are apparently caused by the different composition and crystallized temperature.

(2) Microstructure of the LMFCPAS glass-ceramics

The SEM microstructure of the LMFCPAS glass crystallized at 850 °C for various times is shown in Fig. 2. Fig. 2(a) shows the morphology of the LMFCPAS glass crystallized at 850 °C for 2 h. As indicated by arrows, there are three distinct regions, the dispersed particles region, light-gray region and deep-gray region in this SEM micrograph. The light-gray and deep-gray are presented in narrow strip form. EDS results from three regions in Fig. 2(a) reveal that the deep-gray region primarily contained the ratio of Si 56.30 wt%, Al 26.63 wt%, Ca 5.32 wt% and O 17.45 wt%, whereas the light-gray region primarily contained the ratio of Si 52.50 wt%, Ca 35.00 wt%, O 9.50 wt% and Mn 3.00 wt%. Integrating the results of XRD and EDS, the deep-gray region ((Al, Si)-rich) is identified as the Li2Al2Si3O10 phase and the light-gray region as the β-CaSiO3 phase. Moreover, both β-CaSiO3 and Li2Al2Si3O10 show obviously directional growth. Fig. 2(a) also shows the β-CaSiO3 phase is dominant and the lath structure of β-CaSiO3 breaks and becomes short as the crystallization time increases, as shown in Figs. 2(b) and (c). The Li2Al2Si3O10 phase also appears in a lath structure and is in close contact with the β-CaSiO3.

Fig. 2: SEM microstructure of the LMFCPAS glass crystallized at 850 °C for various lengths of time: (a) 2 h, (b) 8 h, and (c) 16 h.
The SEM microstructure of the 35BaO-35Fe₂O₃-20B₂O₃-10SiO₂-1ZrO₂ (added extra, as a nucleant) (by mol%) glass with one-step heat treatment at 720 °C for 1 h has been observed by Mirkazemi et al. ⁴. They revealed that the BaFe₁₂O₁₉ phase in the crystallized glass sample appeared in diverse crystal shapes and sizes such as small particles, very fine needle-like or platelets with bigger size. Some large sizes of BaFe₁₂O₁₉ with a regular hexagonal shape were also found.

Also based on the one-step crystallization process, both morphologies of β-CaSiO₃ and Li₂Al₂Si₃O₁₀ are found to be different from the droplet shape of the BaFe₁₂O₁₉. In addition, the dendritic structure was also reported in previous results ⁶, but not found in the present study.

Fig. 3 shows the enlarged view of SEM microstructure and EDS result of the LMFCPAS glass crystallized at 850 °C for 16 h. It can be seen that the small particle (as indicated by the arrow) is composed primarily of Mn, Fe, P and O elements. These small particles are identified as the Li(Mn,Fe)PO₄ phase.

Fig. 4 shows the TEM bright field (BF) micrograph and selected area electron diffraction (SAED) patterns of the LMFCPAS glass crystallized at 850 °C for 16 h. Fig. 4(a), the bright field (BF) image, shows the lath and plate structure. Fig. 4(b) is the SAED pattern of the black area on the upper right in Fig. 4(a), the index of which corresponds to FeFe₂O₄ with zone axis of [1 1 4]. Fig. 4(c) shows the SAED pattern of lath form morphology on the right in Fig. 4(a), the index of which corresponds to β-CaSiO₃ with a zone axis of [1 1 0].

Fig. 4: TEM BF micrograph and SAED patterns of a specimen of LMFCPAS glass crystallized at 850 °C for 16 h: (a) BF image, (b) SAED pattern of the lath form structure on the upper right in Fig. 4(a), index corresponding to FeFe₂O₄ with zone axis of [1 1 4], (c) SAED pattern of the lath form structure on the right in Fig. 4(a), index corresponding to β-CaSiO₃ with zone axis of [1 1 0], and (d) SAED pattern index corresponding to Al-Si amorphous.
Fig. 4(d) is the SAED pattern of the white area denoted by the arrow in Fig. 4(a), the index of which corresponds to Al-Si amorphous.

(3) Magnetic properties of the LMFCPAS glass-ceramics

Fig. 5 shows the magnetization curve of the LMFCPAS glass crystallized at 850 °C for 16 h under a magnetic field of 1000 Oe. A very small remnant of magnetic induction and coercive force of 0.01 emu/g and 16 Oe were obtained, respectively. This result showed the ferromagnetic behavior of an inverse spinal structure.

The remnant magnetization and coercive force of 0.71 emu/g and 91 Oe were obtained, respectively, for the 41CaO-42SiO2-10Fe2O3-3Na2O glass crystallized at 1050 °C for 3 h as reported by Singh et al. 3. On the other hand, the coercive force and remnant magnetization were 63 Oe and lower than 0.5 emu/g, respectively, for the 25Li2O-8MnO2-20CaO-2P2O5-45SiO2-8Fe2O3 (added extra) (by mol%) glass crystallized at 850 °C for 4 h under an applied magnetic field of 300 Oe.

Chikazumi et al. 15 reported that a single domain structure in crystalline magnetic phase(s) was formed when the ferrite particle size is in the order of 10 – 50 nm for moderate crystal anisotropy. In addition, the coercive force was affected significantly by the amount and size of the magnetic crystallites in the crystallized glass samples reported by Singh and Srinivasan 13. Comparing the result of present study and results of Hsi et al. 8, it is found that the size of magnetic phases in two studies was in the range of 2 – 3 μm, but the coercive force in the present study is 16 Oe, which is lower than that of 63 Oe in the previous study owing to the appearance of (Li, Mn) ferrite 8. Furthermore, the coercive force and remnant magnetization of the present study were lower than that in the results reported by Singh et al. 3, which could be attributed to the average of magnetic phase of 26 nm only.

The specific absorption rate (SAR) value of heat generation depended on the coercive force and Fe2O3 content. 1, 6 The coercive force of the 25Li2O-8MnO2-20CaO-2P2O5-45SiO2 (by at%) glass with extra addition of 8 at% and 16 at% Fe2O3 (denoted by F3 and F4) crystallized at 850 °C for 4 h was 63 and 100 Oe, respectively and the SAR value was 42.8 and 73.5 W/g, respectively. Although the value of SAR was not measured in the present study, the SAR value of the present study could be suggested to be lower than 42.8 W/g based on the low coercive force of 16 Oe compared with the 63 Oe measured in the previous study. With this lower SAR value, LMFCPAS glass is considered to be a suitable material for a low-heat-generation device.

IV. Conclusions

The phase transformation and magnetic properties of 10Li2O-9MnO2-16Fe2O3-15CaO-5P2O5-5Al2O3-40SiO2 (LMFCPAS) glass have been studied using XRD, SEM, EDS, TEM and SAED. The Li2AlSi3O10, β-CaSiO3 and FeFe2O4 phases were formed when the LMFCPAS glass was crystallized at 750 °C for 2 h. With crystallization at 850 °C for 4 h, Li2AlSi3O10, Li2SiO3, β-CaSiO3, Li3PO4, FeFe2O4 and Li(Mn,Fe)PO4 phases are found and identified in the LMFCPAS glass-ceramics. Both β-wollastonite and lithium silicate exhibited lath morphology and directional growth. The LMFCPAS glass crystallized at 850 °C for 16 h has very low remnant induction (0.013 emu/g) and coercive force (16 Oe) under an applied magnetic field of 1000 Oe, and shows the ferromagnetic behavior of an inverse spinel structure.

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